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Anodic Corrosion of Copper in Presence of Polymers

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***Abstract*— The rates of anodic corrosion of copper plates in different concentration of phosphoric acid (6, 8, 10, 12 and 14 mol) were determined by measuring the limiting current of anodic dissolution. The rates of corrosion were measured in absence and in presence of polyethylene glycol 400, polyethylene glycol 800, polyethylene glycol 4000, polyethylene glycol 6000 (PEG), polyvinyl alcohol 6000 (PVA) and starch. It is found that, the rate of corrosion depends of type of inhabitations and its concentrations. The rate of corrosion decreases by amount ranging from 9.7 to 80.1 % depending on organic compounds and its concentrations. Those compounds verify Langmuir and Flory- Huggins isotherm. Thermodynamic parameters were given.**

***Index Terms*— Electrodeposition, Corrosion Inhibition, Limiting Current, Mass Transfer, Thermodynamic Parameters, Polymers.**

I. INTRODUCTION

Due to its excellent electrical and thermal conductivities and good mechanical workability, copper is a material commonly used in heating and cooling systems. Scales and corrosion products have negative effect on heat transfer and cause decrease in the heating efficiency of equipment, which requires periodic descaling and cleaning in hydrochloric acid pickling solution

Most corrosion inhibitors can eliminate the undesirable destructive effect and prevent metal dissolution. Copper normally does not displace hydrogen from acid solutions and therefore, is virtually not attacked in non-oxidizing conditions. In fact, if hydrogen bubble is passed through a solution of copper salt, it reduces copper as fast as the process occurs **[1]**. Copper dissolution in acidic medium has been studied by several researchers **[2-7]**. Corrosion inhibitors can be used to prevent copper dissolution. Polymers are found to have excellent inhibition properties in several corrosion environments **[8]**. The molecules contain nitrogen atoms and it usually prevents copper by staining and tarnishing [**9**].

One of the most important methods in the protection of copper against corrosion is the use of organic polymer inhibitors [**10**]. Organic compounds containing polar groups including nitrogen, sulfur, oxygen [**11-17**] and heterocyclic compounds with polar functional groups and conjugated double bonds have been reported to inhibit copper corrosion [**18-20**]. The inhibiting action of these organic compounds is usually attributed to their interactions with the copper surface via their adsorption. Polar functional groups are regarded as the reaction center that stabilizes the adsorption process [**21**].

In general, the adsorption of an inhibitor on a metal surface depends on the nature and the surface charge of the metal, the adsorption mode, its chemical structure and the type of electrolyte solution. Polymers are known to be very effective inhibitors for metal and alloys in different corrosion media.

In this study the effect of some polymers on the inhibition of copper corrosion in 8 M H_3PO_4 at different condition has been investigated. The rate of copper corrosion is determined by measuring the anodic limiting current, i.e. at which polishing take place.

II. EXPERIMENTAL PROCEDURE

Materials

Analar grade H_3PO_4 (98% w/w), supplied by BDH chemicals Ltd, was used for preparation of the electrolyte. Six organic polymers (polyethylene glycol 400, polyethylene glycol 800, polyethylene glycol 4000, polyethylene glycol 6000, polyvinyl alcohol 6000 and starch) were used in this work.

Solution Composition

Blank solution consist of 8 M H_3PO_4 Different concentrations from the organic polymers in the range of concentration (10^{-5} - 10^{-2} mol / l) were used.

Apparatus and techniques

Fig. a. represents the cell and the electrical circuit that has been used in this work. The cell consisted of a rectangular plastic container having the dimensions (5.1×5.0×10.0 cm) with electrodes fitting the whole section. Two electrodes, each as rectangular copper plate of 10 cm height and 5 cm width, are located 5.1 cm apart. A porous poly vinyl chloride diaphragm is used to prevent the effect of H_2 bubble. The electrical circuit during this work consisted of 6 Volt D.C. power supply of 6 volt with a voltage regulator and multi-range ammeter was connected in series with cell. Potential differences were obtained by increasing the cell current stepwise and measuring the steady state anode potential against a reference electrode which consisted of a copper wire immersed in a cup of Luggin probe filling with phosphoric acid solution containing organic compound at concentration similar to that in the cell, the tip of Luggin probe is placed 0.5 - 1 mm tube from the anode surface. The Potential difference between the anode and the reference electrode is measured by high impedance potentiometer. Ortho-phosphoric acid concentration is prepared from Analar ortho-phosphoric acid and distilled water. The anode height is 2 cm. before each run the block part of the anode is insulated with poly-styrene lacquers and the active surface of the anode is polished with fine emery paper, degreased with trichloroethylene, Washed with alcohols and finally rinsed in distilled water. Electrode treatment is similar to that used by Wilke[29]. The rate of copper corrosion under different conditions is determined by measuring the limiting Current at 25°C.

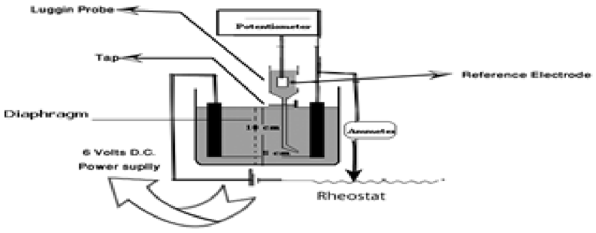

Fig. a. Schematic diagram of the apparatus

III. RESULTS AND DISCUSSION

Leveling process

Fig. 1- 3 and Table 1 show the polarization curves for the copper electrode in 8 M H_3PO_4 solutions in presence of different concentrations of polyethylene glycol 400 and starch, respectively, using divided cell at 25°C.

The limiting current at which polishing take place was determined from those polarization curves and used to calculate the mass transfer coefficient (K) of copper polishing in H_3PO_4 from the equation:

$$K = I / zFC_o \qquad (1)$$

where,
I: limiting current, mA.
F: Faraday constant.
C_o: concentration of saturated copper phosphate.
z: valency.

The values of the limiting current for all compounds at different temperatures are given in Table1. Leveling is the principle process in electropolishing **[22].**

Mayer explained the necessity to separate between anode and cathode by non-conductive slit to prevent the gas bubbles transfer to the anode surface and to enhance the homogenous distribution of electric current **[23]**. The study of leveling is based on the classical current voltage curves of electropolishing as shown in Figs. 1-3 typical polarogram obtained in this study for polymers in case of divided cell.

Table 1. The values of limiting current (mA) at different temperatures for all compounds used in case of divided cell.

Conc.	**Polyethylene glycol 400**				**Polyethylene glycol 6000**			
$M*10^6$	**25°C**	**30°C**	**35°C**	**40°C**	**25°C**	**30°C**	**35°C**	**40°C**
0.0	710	750	800	860	710	750	800	860
0.5	650	670	720	730	570	585	600	620
1.0	580	600	630	640	540	540	555	570
1.5	550	570	590	610	490	510	530	545
2.0	510	530	540	550	460	480	500	520
2.5	470	485	500	530	420	435	450	470
3.0	430	445	460	500	390	405	420	430
5.0	405	420	435	450	275	290	310	330
Conc.	**Polyethylene glycol 800**				**Polyvinyl alcohol 6000**			
$M*10^6$	**25°C**	**30°C**	**35°C**	**40°C**	**25°C**	**30°C**	**35°C**	**40°C**
0.0	710	750	800	860	710	750	800	860
0.5	620	640	660	680	550	570	585	600
1.0	565	585	600	620	520	540	555	570
1.5	530	545	560	580	490	500	510	520
2.0	485	500	515	570	430	445	450	465
2.5	460	470	480	490	410	425	440	450
3.0	425	440	455	470	370	380	390	405
5.0	385	400	410	420	210	230	250	280
Conc.	**Polyethylene glycol 4000**				**Starch**			
$M*10^6$	**25°C**	**30°C**	**35°C**	**40°C**	**25°C**	**30°C**	**35°C**	**40°C**
0.0	710	750	800	850	710	750	800	860
0.5	590	610	630	650	510	530	550	570
1.0	550	470	580	600	480	495	510	530
1.5	510	525	540	550	420	435	450	470
2.0	470	480	490	500	370	385	400	420
2.5	450	460	470	480	300	320	340	350
3.0	400	410	420	440	240	260	280	300
5.0	350	370	385	400	145	160	180	200

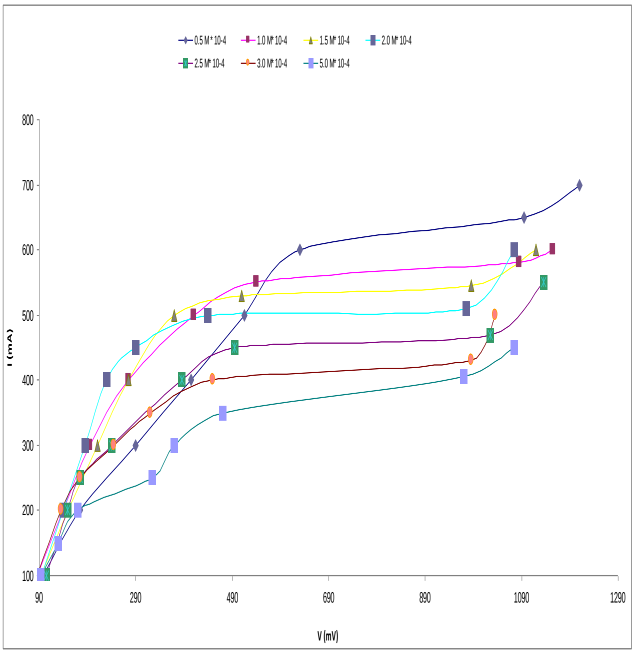

Fig. 1. The relation between I (mA) and V (mV) in presence of polyethylene glycol 400 at 25ºC and 8 M H_3PO_4 for divided cell at 1 cm height.

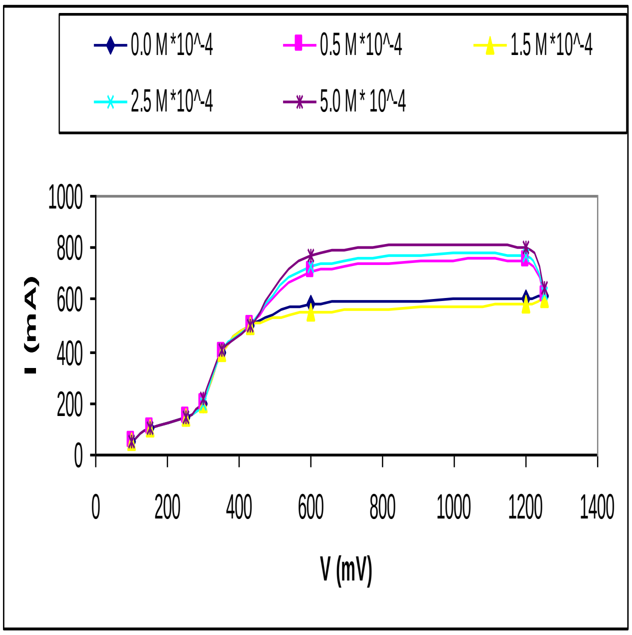

Fig. 2. The relation between I (mA) and V (mV) in presence of polyethylene glycol 800 at 25ºC and 8 M H_3PO_4 for divided cell at 1 cm height.

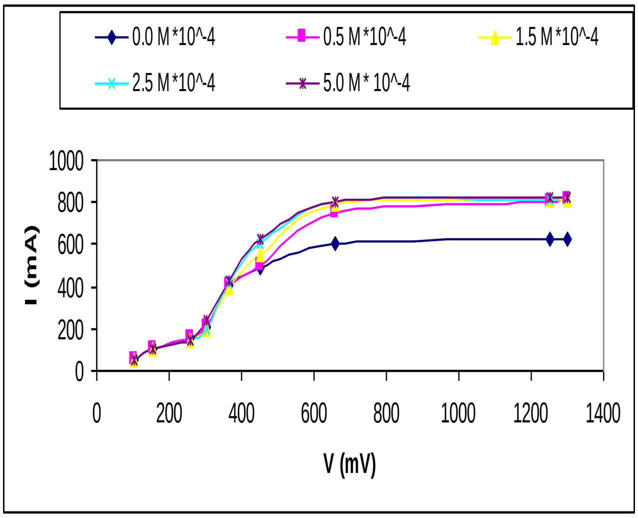

Fig. 3. The relation between I (mA) and V (mV) in presence of polyethylene glycol 4000 at 25ºC and 8 M H_3PO_4 for divided cell at 1 cm height.

Effect of organic compounds concentration on the limiting current

The rate of electropolishing which is represented by the anodic limiting current decreases with increasing the concentration of organic additives as shown in Table 2. It is recommended, on the basis of results, that it may use in this range of concentration to inhibit the corrosion of copper metal in 8 M H_3PO_4 acid in presence of organic compounds to be used in this work **[24].**

The mass transfer coefficient of polishing process, which is used in data correlation, is calculated from the limiting current using the equation:

$$K= I/zFAC_s \qquad (2)$$

The above equation is based on the finding of previous studies **[25].**

The percentage of inhibition, % IE, can be calculated from the following equation:

$$\% IE = I-I_l/I \times 100 \qquad (3)$$

where :

I and I_l are the limiting current densities in absence and presence of the organic compounds

Fig. 4. and Table 2 show that the percent inhibition caused by organic compounds ranges from 9.7% to 80.1% depending on the organic compounds and their concentration.

The limiting current decreases with increasing the concentration of polymers which agrees with the findings of other authors who worked within the same range of concentration using other inhibitors [**26]**.

The decrease in the limiting current with increasing the concentration of organic compounds is attributed to:

(a) The solubility of dissolved copper phosphate in ortho phosphoric acid, which is responsible for the limiting current, decreases with increasing organic compound concentration.

(b) The viscosity of the solution increases with increasing polymers concentration with consequence decrease in the diffusivity of' Cu^{2+} according to Stokes-Einstein equation **[27].**

Table 2. The relation between percentage inhibition and concentration of all compounds at 25°C.

C x 10^5 mol.l^{-1}	% Inhibition					
	Polyethylene glycol 400	Polyethylene glycol 800	Polyethylene glycol 4000	Polyethylene glycol 6000	Polyvinyl alcohol 6000	Starch
0.5	9.7	13.9	18.1	20.8	23.6	29.2
1.0	19.4	21.5	23.6	25.0	27.8	33.3
1.5	23.1	26.4	29.2	31.9	40.3	48.6
2.0	29.2	32.6	34.7	36.1	40.3	48.6
2.5	34.7	36.1	37.5	41.7	43.1	58.3
3.0	40.2	40.9	41.7	45.8	48	66.7
5.0	43.8	46.5	51.4	61.8	70.8	80.1

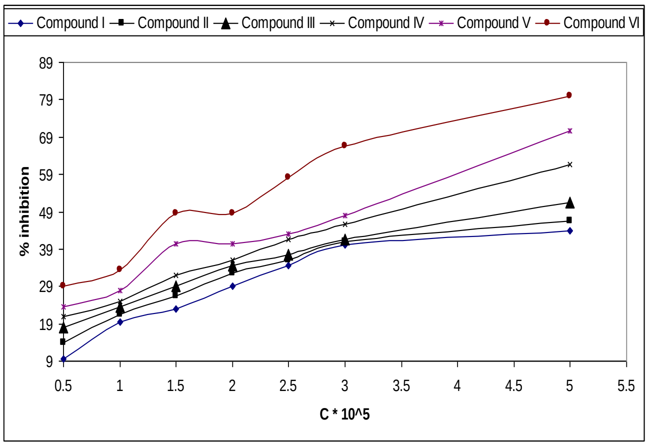

Fig.4. The relation between % inhibition and concentration of all compounds at 25°C.

Adsorption Isotherm

The values of I obtained at different temperatures permits the calculation of activation energy E_a according to Arrhenius equation:

$$\log I = -E_a/2.303\ RT + \log A \qquad (4)$$

The plot of log I against 1/T gave a straight line where A is pre-exponential factors R the gas constant and T is absolute temperature.

The slope of the straight line is proportional to E_a. the activation energy of process is an important parameters to determining the rate controlled step. If the rate controlling step is diffusion of species in boundary layer E_a is generally $\leq$ 28 kj/mole while E_a usually > 43 kj/mole when reaction is chemically controlled.

Table 6 and 7 shows that the values of E_a are lower than 43.3 kj/mole characterizing diffusion process to controlling electroplating process.

Application of Langmuir isotherm

Inhibitor adsorption characteristics can be estimated by using the Langmuir isotherm given by the following equation [**28**]:

$$KC = \theta/1-\theta \qquad (5)$$

$$\theta = I_b - I/\ I_b \qquad (6)$$

where:

θ : is the part of surface covered with adsorbed organic compound.

C : is the concentration of organic compound, $mol.cm^{-3}$.

I : is the limiting current in presence of organic compound.

I_b : is the limiting current in absence of organic compound.

K : is the Langmuir constant.

Plot of θ / (1- θ) against C should yield a straight line. Table 3 gives the data of θ, θ / (1- θ) and C for all polymers and the surface coverage with concentration variation for divided cell.

From above, it is concluded that all compounds verify Langmuir Isotherm show in Figs. 5 to 10.

Figs.11 to 16 shows the Flory-Huggins adsorption isotherm for electropolishing in H_3PO_4 plotted as log θ /C against log (1- θ) at 25°C. A straight line is obtained with a slope x and intercept log xK.

The experimental data fit the Flory-Huggins adsorption isotherm which is represented by:

$$\log \theta /C = \log xK + x\log (1-\theta) \qquad (7)$$

where x is the number of water molecules replaced by one molecule of the inhibitor. It is clear that the surface coverage data are useful for discussing adsorption characteristics.

The adsorption of inhibitors at metal/solution interface may be due to the formation of either electrostatic or covalent bonding between the adsorbents and the metal surface atoms **[29]**.

The kinetic adsorption isotherm may be written in the form:

$$\log \theta /1-\theta = \log k' + y \log C \qquad (8)$$

where y is the number of inhibitor molecules occupy one active site. The binding constant of adsorption $K= k'^{1/y}$, where 1/y is the number of the surface active sites occupied by one molecule of the inhibitor, and k is the binding constant.

Figs. 17 to 22 show the relation between log θ /1- θ and log C at 25°C, and the calculated values of 1/y and K are given in Table 4.

The values of 1/y depend on the type of polymers derivatives. From Table 4 it is obvious that the value of 1/y for polymers derivatives is approximately one suggesting that the compound attached to one active site per inhibitor molecule.

For other inhibitors, the values of 1/y are higher than one, indicating that, the given inhibitors molecules attached to more than one active site. The free energy of adsorption (ΔG_{ads}) at different concentration is calculated from the following equation:

$$\Delta G_{ads} = -\ RT\ln\ (55.5K) \qquad (9)$$

Table 3. The data for adsorption isotherm of copper at 25°C for different polymers

Conc. $M*10^4$	% Inh.	log C	Θ	Θ /1- Θ	log(Θ /1- Θ)	1- Θ	log(1- Θ)	log Θ /C
Polyethylene glycol 400								
0.5	9.72	-4.30	0.097	0.108	-0.97	0.92	-0.04	3.29
1.0	19.44	-4.00	0.194	0.241	-0.62	0.81	-0.09	3.28
1.5	23.61	-3.82	0.236	0.309	-0.51	0.76	-0.12	3.20
2.0	29.17	-3.70	0.292	0.412	-0.39	0.71	-0.15	3.16
2.5	34.72	-3.60	0.347	0.532	-0.27	0.65	-0.19	3.14
3.0	40.28	-3.52	0.402	0.674	-0.17	0.60	-0.22	3.13
5.0	43.75	-3.30	0.438	0.778	-0.11	0.56	-0.25	2.94
Polyethylene glycol 800								
0.5	13.89	-4.30	0.139	0.161	-0.79	0.85	-0.07	3.44
1.0	21.53	-4.00	0.215	0.274	-0.56	0.78	-0.11	3.33
1.5	26.39	-3.80	0.264	0.358	-0.45	0.74	-0.13	3.25
2.0	32.64	-3.70	0.326	0.485	-0.315	0.68	-0.17	3.21

2.5	36.11	-3.60	0.361	0.565	-0.25	0.65	-0.19	3.16
3.0	40.97	-3.52	0.409	0.694	-0.16	0.60	-0.22	3.13
5.0	46.53	-3.30	0.465	0.870	-0.06	0.54	-0.27	2.97
Polyethylene glycol 4000								
0.5	9.72	-4.30	0.097	0.108	-0.97	0.92	-0.04	3.29
1.0	19.44	-4.00	0.194	0.241	-0.62	0.81	-0.09	3.28
1.5	23.61	-3.82	0.236	0.309	-0.51	0.76	-0.12	3.20
2.0	29.17	-3.70	0.292	0.412	-0.39	0.71	-0.15	3.16
2.5	34.72	-3.60	0.347	0.532	-0.27	0.65	-0.19	3.14
3.0	40.28	-3.52	0.402	0.674	-0.17	0.60	-0.22	3.13
5.0	43.75	-3.30	0.438	0.778	-0.11	0.56	-0.25	2.94
Polyethylene glycol 6000								
0.5	13.89	-4.30	0.139	0.161	-0.79	0.85	-0.07	3.44
1.0	21.53	-4.00	0.215	0.274	-0.56	0.78	-0.11	3.33
1.5	26.39	-3.80	0.264	0.358	-0.45	0.74	-0.13	3.25
2.0	32.64	-3.70	0.326	0.485	-0.315	0.68	-0.17	3.21
2.5	36.11	-3.60	0.361	0.565	-0.25	0.65	-0.19	3.16
3.0	40.97	-3.52	0.409	0.694	-0.16	0.60	-0.22	3.13
5.0	46.53	-3.30	0.465	0.870	-0.06	0.54	-0.27	2.97
Polyvinyl alcohol 6000								
0.5	9.72	-4.30	0.097	0.108	-0.97	0.92	-0.04	3.29
1.0	19.44	-4.00	0.194	0.241	-0.62	0.81	-0.09	3.28
1.5	23.61	-3.82	0.236	0.309	-0.51	0.76	-0.12	3.20
2.0	29.17	-3.70	0.292	0.412	-0.39	0.71	-0.15	3.16
2.5	34.72	-3.60	0.347	0.532	-0.27	0.65	-0.19	3.14
3.0	40.28	-3.52	0.402	0.674	-0.17	0.60	-0.22	3.13
5.0	43.75	-3.30	0.438	0.778	-0.11	0.56	-0.25	2.94
Starch								
0.5	13.89	-4.30	0.139	0.161	-0.79	0.85	-0.07	3.44
1.0	21.53	-4.00	0.215	0.274	-0.56	0.78	-0.11	3.33
1.5	26.39	-3.80	0.264	0.358	-0.45	0.74	-0.13	3.25
2.0	32.64	-3.70	0.326	0.485	-0.315	0.68	-0.17	3.21
2.5	36.11	-3.60	0.361	0.565	-0.25	0.65	-0.19	3.16
3.0	40.97	-3.52	0.409	0.694	-0.16	0.60	-0.22	3.13
5.0	46.53	-3.30	0.465	0.870	-0.06	0.54	-0.27	2.97

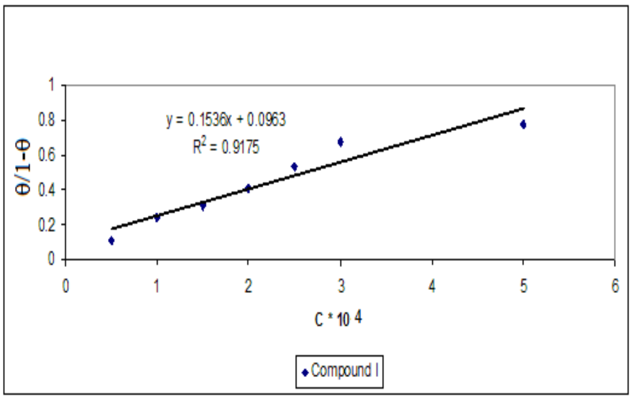

Fig. 5. Langmuir adsorption isotherm for polyethylene glycol 400.

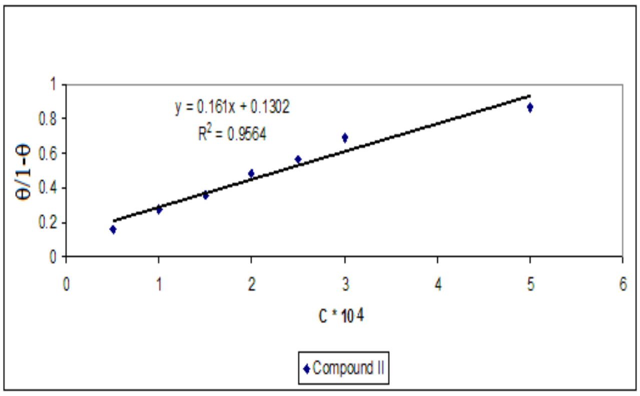

Fig. 6. Langmuir adsorption isotherm for polyethylene glycol 800.

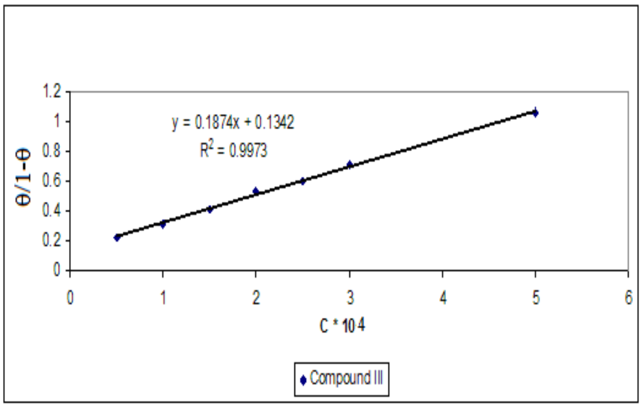

Fig. 7. Langmuir adsorption isotherm for polyethylene glycol 4000.

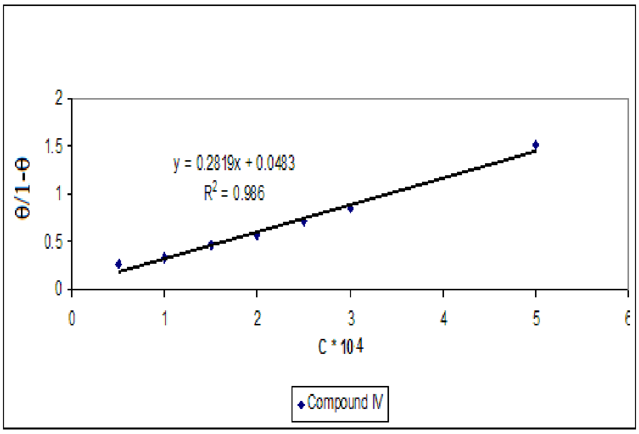

Fig. 8. Langmuir adsorption isotherm for polyethylene glycol 6000.

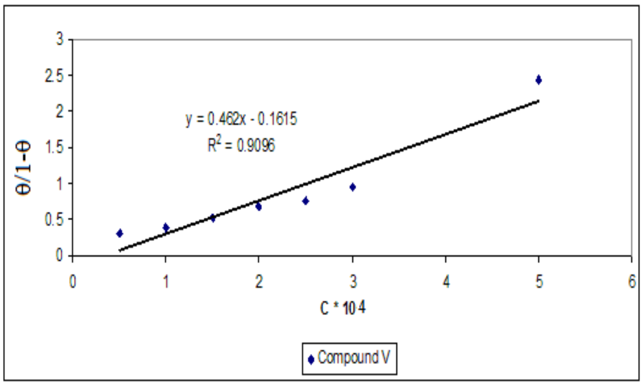

Fig. 9. Langmuir adsorption isotherm for polyvinyl alcohol 6000.

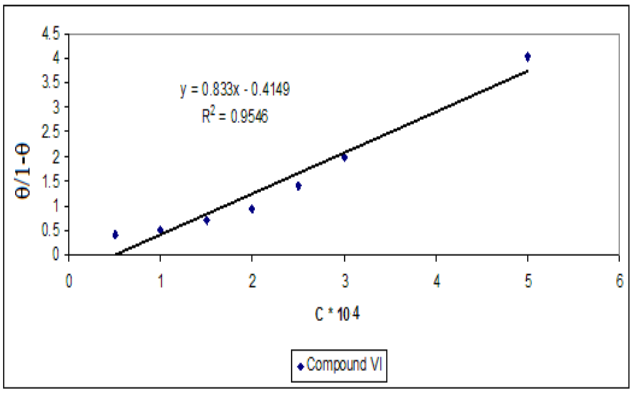

Fig. 10. Langmuir adsorption isotherm for starch.

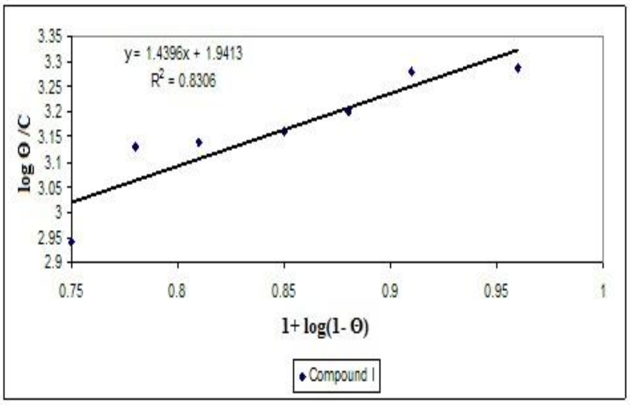

Fig. 11. Flory-Huggins adsorption isotherm at 25ºC for polyethylene glycol 400 **.**

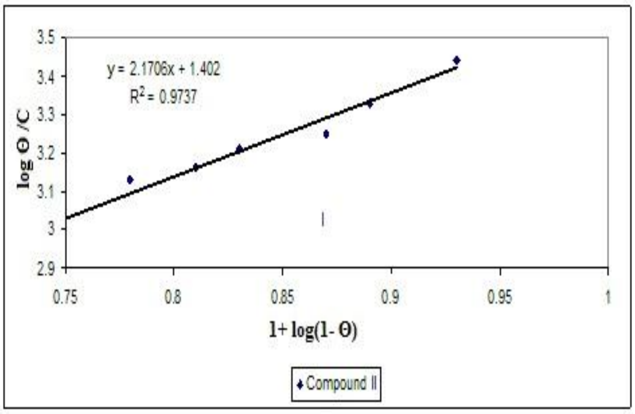

Fig. 12. Flory-Huggins adsorption isotherm at 25ºC for polyethylene glycol 800 **.**

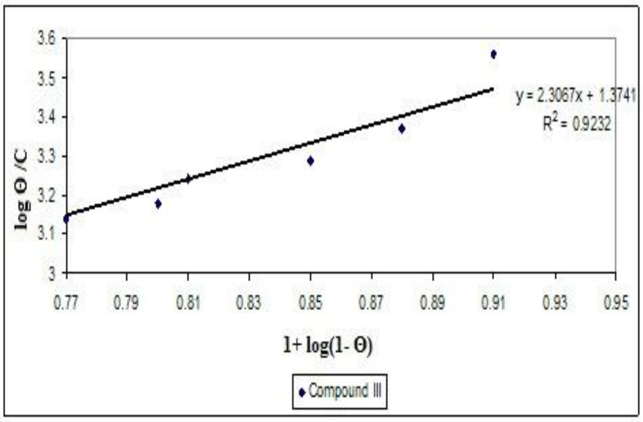

Fig. 13. Flory-Huggins adsorption isotherm at 25ºC for polyethylene glycol 4000.

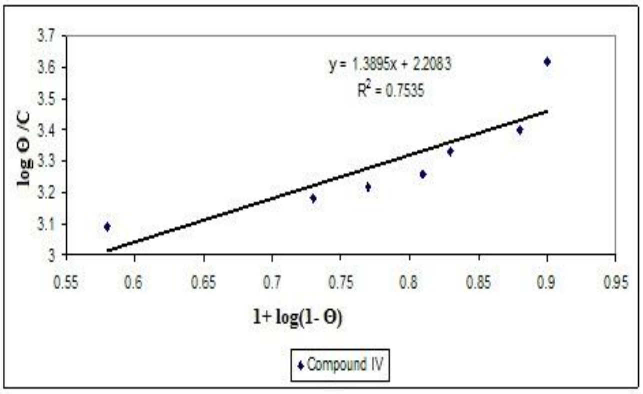

Fig. 14. Flory-Huggins adsorption isotherm at 25ºC for polyethylene glycol 6000.

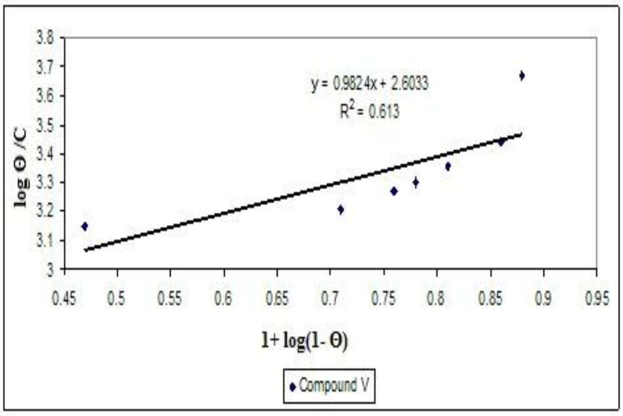

Fig. 15. Flory-Huggins adsorption isotherm at 25ºC for polyvinyl alcohol 6000.

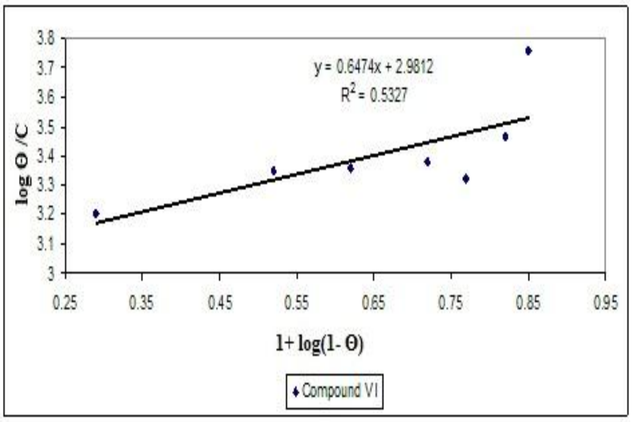

Fig. 16. Flory-Huggins adsorption isotherm at 25ºC for starch.

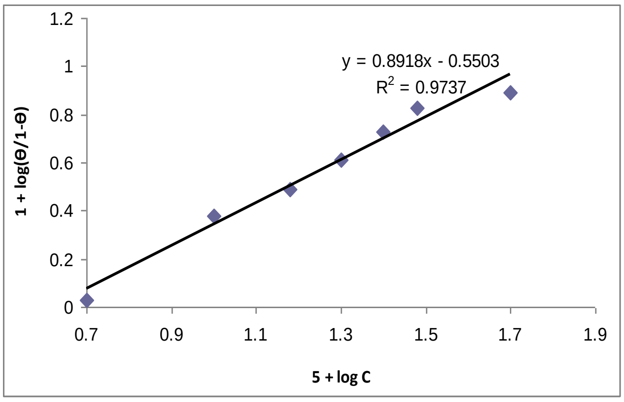

Fig. 17. Kinetic adsorption isotherm for polyethylene glycol 400 at 25ºC.

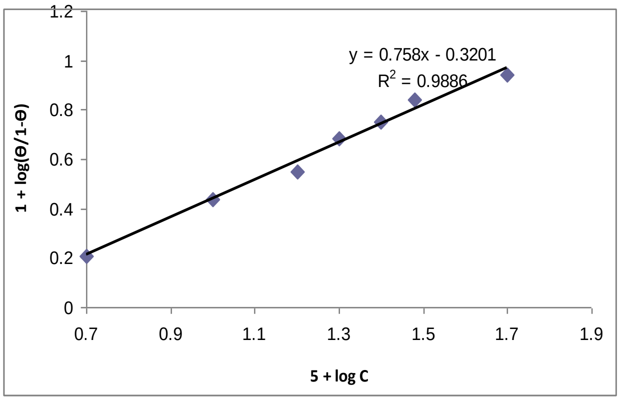

Fig. 18. Kinetic adsorption isotherm for polyethylene glycol 800 at 25ºC.

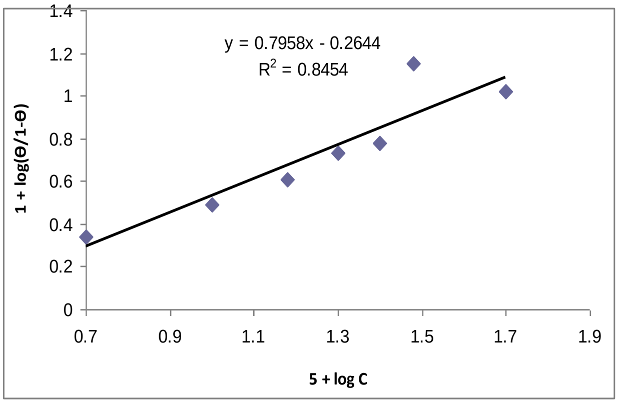

Fig. 19. Kinetic adsorption isotherm for polyethylene glycol 4000 at 25ºC.

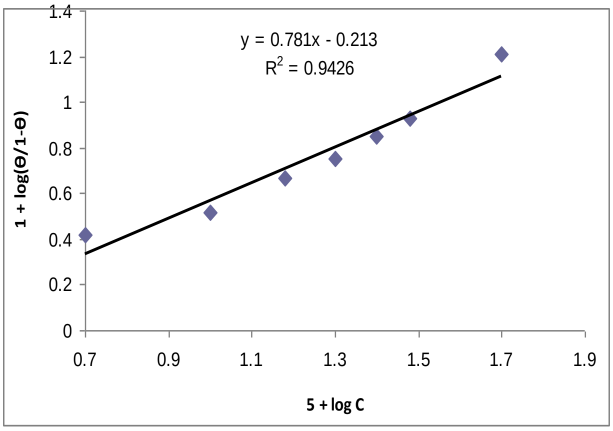

Fig. 20. Kinetic adsorption isotherm for polyethylene glycol 6000 at 25ºC.

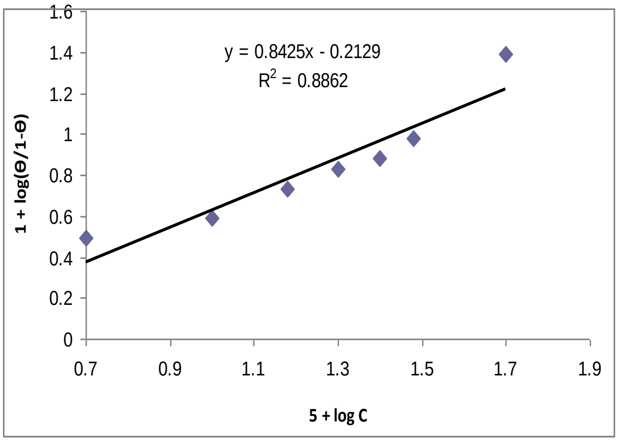

Fig. 21. Kinetic adsorption isotherm for polyvinyl alcohol 6000 at 25ºC.

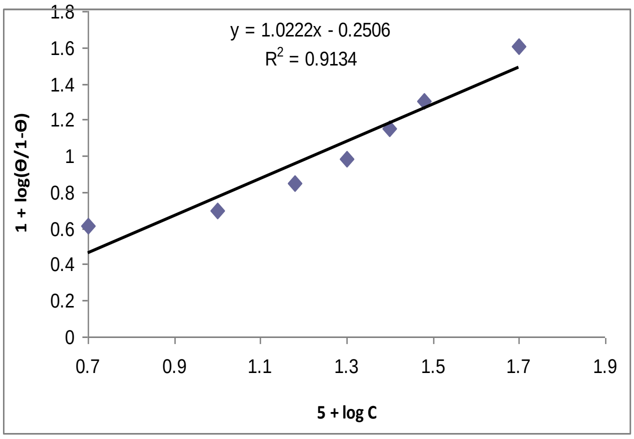

Fig. 22. Kinetic adsorption isotherm for starch at 25ºC.

The value 55.5 is the concentration of water in the solution mol/1. The values of ΔG_{ads} are giving in Table 5.

In all cases, the ΔG_{ads} values are negative and lie in the rank of 5.37 - 31.31 k.J/mol. The most efficient inhibitor shows the most negative value. This suggests that they are strongly adsorbed on the metal surface. The negative values of ΔG_{ads} indicate the spontaneous adsorption of the inhibitor. It is found that the ΔG_{ads} values are more positive than - 40 k.J/mol indicating that the inhibitors are physically adsorbed on the metal surface. Similar results also have been reported [**30].**

Table 4. The values of k, x and 1/y of phosphoric acid in presence of different organic polymers to Langmuir, Flory-Huggins and Kinetic adsorption isotherm.

Compounds	Flory-Huggins		Kinetic adsorption isotherm			Langmuir
	X	K	Y	1/y	K	K
Polyethylene glycol 400	1.4396	1669.39	0.8918	1.12	810.59	0.154
Polyethylene glycol 800	2.1706	1721.95	0.7572	1.32	294.04	0.161
Polyethylene glycol 4000	1.8727	2027.83	0.6903	1.45	188.93	0.187
Polyethylene glycol 6000	1.4195	2913.83	0.7810	1.28	491.81	0.282
Polyvinyl alcohol 6000	2.3713	2980.67	0.8425	1.19	997.01	0.462
Starch	0.6374	2682.53	0.9858	1.01	5640.09	0.833

Table 5. The values of free energy of adsorption (kJ. mol^{-1}) of phosphoric acid in presence of different organic polymers using different methods.

Compounds	$-\Delta G_{ads}$		
	Flory-Huggins	Kinetic adsorption isotherm	Langmuir
Polyethylene glycol 400	28.35	26.56	5.375
Polyethylene glycol 800	28.42	24.04	5.470
Polyethylene glycol 4000	28.83	22.95	5.810
Polyethylene glycol 6000	29.73	25.32	6.870
Polyvinyl alcohol 6000	29.78	27.07	8.100
Starch	29.52	31.36	9.600

Effect of temperature

The effect of temperature on the Cu electropolishing rate in absence and presence of polymers was determined in the temperature range 25, 30, 35, 40°C as illustrated in Table 1.

It is observed that the electropolishing rate increases with rise in temperature for different concentrations of organic compounds, because adsorption of polymers on copper anode decreases by increasing temperature.

Thermodynamic treatment of the results

From the integrated form of the Arrhenius equation:

$$\ln I = - E_a/RT + \ln A \qquad (10)$$

where R is the gas constant (8.314 $kJmol^{-1}$), E_a is the activation energy and A is the frequency factor it can be seen that the gradient is given by $-E_a/R$ and the intercept by ln A. Tables 6 and 7 gave the values of E_a for the compounds used. The values for enthalpy of activation ΔH^*, entropy of activation ΔS^*, and free energy of activation ΔG^* can also be obtained by using the following equations and are given in Tables 6 and 7.

$$\Delta H^* = E_a - RT \qquad (11)$$

$$\Delta S^* / R = \ln A - \ln (kTe/h) \qquad (12)$$

$$\Delta G^* = \Delta H^* - T\,\Delta S^* \qquad (13)$$

where:

k : is Boltzmann's constant.

e : = 2.7183.

h : is Plank's constant.

A : is Arrhenius constant.

T : is absolute temperature, °K.

R : is the universal gas constant=8.314$Jmol^{-1}K^{-1}$.

The adsorption is usually followed by liberation of heat of adsorption, so that $E_a < 0$, consequently the rate of adsorption decreases with rise in temperature and as a result, the surface coverage at given concentration decreases with raising temperature.
It is known that an increase in the heat of adsorption leads to an increase in the energy of adsorption. However, rising of the temperature acts in the reverse direction, increasing the kinetic energy of the molecules, facilitating disruption (consequently in the physical adsorption).
In absence of organic substance, the results fit a straight line with an activation energy equals to 31.935 k.J.mol^{-1} which is higher than the values obtained when organic substance was used as inhibitor.

Thus, the low values of activation energy show that:

[1] The rate of electropolishing of copper from phosphoric acid decreases by adding small amounts of the organic substances **[31]** at temperature above 25°C.

[2] The adsorption process is physical adsorption and the molecules of organic substance are disrupted at temperature above 30°C completely.

Tables 6 and 7 show that the entropy ΔS^* possess height negative values indicating a highly ordered organic species in the solution under investigation. These values found to be independent on the type of polymers.

Table 6. The values of activation energy and thermodynamic parameters for polyethylene glycol 400 to polyethylene glycol 4000.

Organic substances	C x 10^5 mol.l^{-1}	Thermodynamic Parameters			
		E_a (kJ.mol^{-1})	ΔH^* (kJ.mol^{-1})	ΔG^* (kJ.mol^{-1})	- ΔS^* (J.mol^{-1} k^{-1})
Polyethylene glycol 400	0.5	5.358 ± 0.003	2.88 ± 0.003	5.74± 0.006	182± 10
	1.0	8.538 ± 0.002	3.17 ± 0.006	57.5 ± 0.012	182 ± 2.1
	1.5	7.240 ± 0.288	4.77 ± 0.023	57.8 ± 0.57	177 ± 0.9
	2.0	6.780 ± 0.023	4.30 ± 0.0023	57.9 ± 0.075	180 ± 7.8
	3.0	9.033 ± 0.002	7.78 ± 0.0042	58.4 ± 0.084	178 ± 14
	5.0	18.460 ± 0.501	16.00 ± 0.501	59.75 ± 0.991	141.8 ± 1.64
Polyethylene glycol 800	0.5	4.78 ± 0.034	2.303 ± 0.034	57.1± 0.006	183.7 ± 1.1
	1.0	4.85 ± 0.023	2.37 ± 0.023	53.3 ± 0.46	184± 7.6
	1.5	9.521 ± 0.04	3.13 ± 0.04	57.17 ± 0.9	211 ± 15.5
	2.0	5.61 ± 0.272	3.13 ± 0.21	57.17 ± 0.518	180± 8.5
	3.0	10.92 ± 2.9	8.44 ± 2.9	58.1 ± 0.55	166 ± 9.5
	5.0	6.67 ± 0.299	4.164 ± 0.299	58.2 ± 0.591	181 ± 9.6
Polyethylene glycol 4000	0.5	9.2 ± 0.023	6.71 ± 0.23	57.36± 4.6	176 ± 7.6
	1.0	6.62 ± 0.02	6.141 ± 0.02	58.38 ± 0.04	178.5± 6.8
	1.5	5.71 ± 0.008	3.281± 0.08	57.6 ± 0.017	182 ± 2.8
	2.0	7.93 ± 0.09	5.45 ± 0.09	57.9 ± 0.032	181 ± 2.8
	3.0	7.41± 0.95	4.93 ± 0.033	58.3 ± 0.07	179 ± 11.1
	5.0	9.78 ± 0.98	7.3 ± 0.98	59 ± 3.5	173 ± 5.6

Table 7. The values of activation energy and thermodynamic parameters for polyethylene glycol 6000 to starch.

Organic substances	C x 10^5 mol.l^{-1}	Thermodynamic Parameters			
		E_a (kJ.mol^{-1})	ΔH^* (kJ.mol^{-1})	ΔG^* (kJ.mol^{-1})	- ΔS^* (J.mol^{-1} k^{-1})
Polyethylene glycol 6000	0.5	8.88 ± 0.048	4.083 ± 0.048	57.574± 0.925	179 ± 1.53
	1.0	6.10 ± 0.013	3.621± 0.013	57.71 ± 0.026	181.4 ± 4
	1.5	1.621 ± 0.02	0.857 ± 0.02	57.86 ± 5.8	196.9 ± 9
	2.0	8.85 ± 0.741	6.371 ± 0.741	58.86 ± 5.1	162 ± 14
	3.0	11.554 ± 0.152	9.08± 0.152	59.43 ± 0.30	168 ± 4.9
	5.0	14.67± 0.81	12.196 ± 0.8	59.7 ± 2.7	159 ± 4.6
Polyvinyl alcohol 6000	0.5	4.58± 0.006	2.1 ± 0.006	57± 0.013	184 ± 2.1
	1.0	5.1 ± 0.044	2.621 ± 0.044	57.2 ± 0.0087	183.2± 1.4
	1.5	5.36± 0.003	2.88 ± 0.003	57.4± 0.006	183.0 ± 10
	2.0	5.76 ± 0.008	3.28 ± 0.008	57.6 ± 0.0017	182.0 ± 2.8
	3.0	11.16 ± 0.21	8.68 ± 0.21	57.8 ± 0.57	164.8 ± 9.55
	5.0	6.65 ± 0.3	4.17± 0.3	58.2 ± 0.59	181± 9
Starch	0.5	5.915 ± 0.416	2.98 ± 0.0416	57.278± 0.90	182.6 ± 1.5
	1.0	5.459 ± 0.006	2.98 ± 0.006	57.42 ± 0.013	182.6 ± 2.15
	1.5	6.96 ± 0.247	4.482 ± 0.0247	57.66 ± 0.541	178.3 ± 0.89
	2.0	6.347 ± 0.016	4.483 ± 0.016	57.821 ± 0.032	181 ± 5.39
	3.0	7.411 ± 0.035	4.932 ± 0.035	58.2 ± 0.115	178.7 ± 0.11
	5.0	9.778 ± 1.77	7.299 ±1.77	59.063± 3.513	± 5.8

IV. CONCLUSION

The rate of electropolishing of anodic dissolution is determined by measuring limiting current. It is found that the rate of anodic corrosion decreases in presence of polymers. Rate of inhibition depends on concentration of organic substance and rate of corrosion increases by increasing temperature.

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